Scanning and energy dispersive EXAFS studies of ethyl transmetallation in an alkene oligomerisation catalyst

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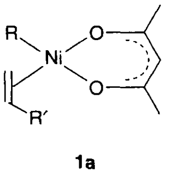
Nickel K-edge XAS studies show that there is a rapid alkyl and β-diketonate exchange between [Ni(acac)$_2$] and AlEt$_2$(OEt) with [NiR(alkene)(acac)] as the main species present under catalytic conditions.

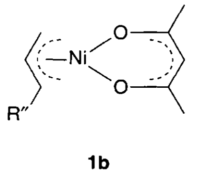
Previously some of us have shown that the activation of nickel catalysts for alkene oligomerisation catalysis can be followed by X-ray absorption spectroscopy (XAS).[1–3] Our attention was drawn by a report by Jones and Symes[4] of a catalyst for the linear dimerisation of hex-1-ene since it was reported to form yellow–brown active and green inactive solutions, with the latter containing [Ni(acac)$_2$] and being favoured below 0 °C. Here we report scanning and energy dispersive XAS experiments which show there is a rapid equilibrium involving alkyl transfer between the precursor (Ni) and promoter (Al) metals.

Ni K-edge XAS data were recorded on a mixture of [Ni(acac)$_2$] (70 mmol dm^{-3}), AlEt$_2$(OEt) and hex-1-ene (Ni : Al : hexene = 1 : 2 : 20) in toluene at −70 and 5 °C, according to reported procedures.[3]† At the lower temperature, analysis showed the presence of 5.6(2) Ni–O bonds [1.975(5) Å] and 0.8(2) Ni–Ni bonds [2.82(1) Å], consistent with the presence of [Ni(acac)$_2$]$_3$. The near-edge structure displayed the white-line feature characteristic of this complex. The spectrum at 5 °C, however, was best analysed in terms of one acac ligand [2.0(4) Ni–O at 1.92(1) Å and 2.0(4) Ni···C at 2.90(2) Å] and three carbon donors [3.1(4) Ni–C at 2.025(4) Å]. Two alternative structures based on these data are **1a** or **1b** (R, R′ and R″ mixed alkyls derived from Al–Et and hexene). Addition of PEt$_3$ (Ni : P = 1 : 1) maintains the acac unit [2.6(2) Ni–O 1.89(1) Å, 1.9(3) Ni···C 2.80(2) Å], but reduces the number of first-row atoms by 2 (a separate Ni–C shell could not be fitted with statistical significance and hence the Ni–O shell incorporates Ni–C also), replacing them with an Ni–P bond [1.1(1) Ni–P at 2.109(3) Å]. This would fit with the reaction of Scheme 1 involving **1a**.

In order to learn more about the transmetallation reaction, and to test the applicability of time-resolved EXAFS (extended X-ray absorption fine structure) spectroscopy, we carried out energy dispersive EXAFS (EDE) with a modified version of a low-temperature cell[3,5] now fitted with a pair of syringe drivers to provide a continuous or interrupted flow mixing. These were triggered outside the hutch of Station 9.3. The detector system comprised a 512 element linear photodiode array (PDA) RL0512T running with a minimum read-out time of 2 ms and controlled by a VM-based system. Recent detector developments[8] have provided a linearity of better than 0.3% over the full dynamic range. The ultra low-noise amplifier and read-out, together with an accurate I_0 normalisation have allowed this type of experiment to be feasible for the first time. The Ni K-edge X-ray absorption spectrum of [Ni(acac)$_2$]$_3$ in toluene (100 mmol dm^{-3}) was acquired in 14.5 s (average of 1000 × 14.5 ms scans); the EXAFS data analysis agrees closely with that derived from the scanning XAS experiments.

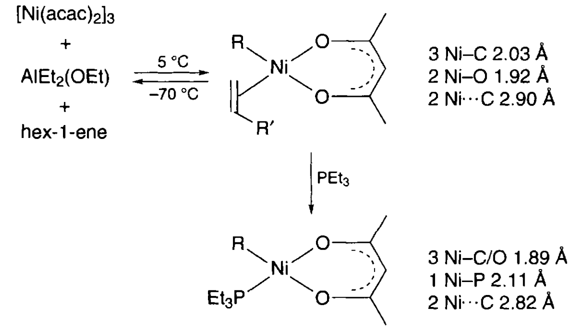


1a



1b

Solutions of [Ni(acac)$_2$] (140 mmol dm^{-3}) and hex-1-ene (Ni : hexene = 1 : 20) were added to a solution of AlEt$_2$(OEt) (280 mmol dm^{-3}) in toluene. Spectra were acquired over a range of *ca.* 8250–8750 eV in 2.0 s (average of 100 acquisitions of 20 ms duration) with a cycle time of 10–15 s. Monitoring the UV–VIS spectra of this reaction at room temperature showed a



Scheme 1 Scheme for the reaction of [Ni(acac)$_2$]$_3$ with AlEt$_2$(OEt) and hex-1-ene

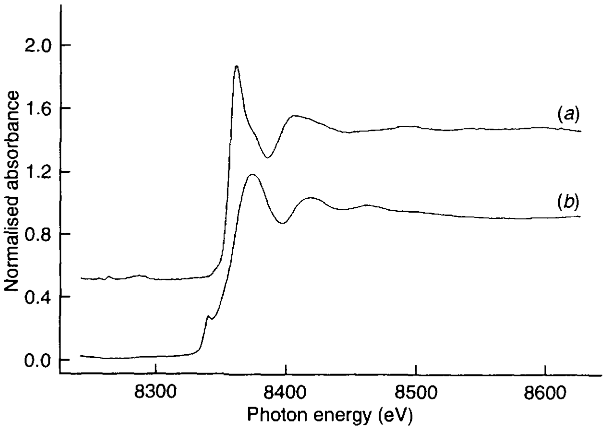


Fig. 1 The Ni K-edge background subtracted absorption spectra of a solution of [Ni(acac)$_2$], AlEt$_2$(OEt) (Ni : Al = 1 : 2) and hex-1-ene (Ni : hexene = 1 : 20) in toluene showing (*a*) the EDE data obtained in 14.5 s after 4.75 min at 0 °C and (*b*) the scanning XAS obtained over 3 h at 5 °C

growth in an absorption band at 391 nm within 30 s, followed by slower changes (20 min) manifest at 485 nm. Analysis of various sequences of EDE shows that the extent of reaction was greater at larger Al : Ni ratios and higher temperatures. It also indicates that the approach to the initial equilibrium is rapid (within 40 s at 0 °C). Fig. 1 compares the XAS spectra of the spectrum obtained by scanning and EDE techniques. The 'white-line' feature has reduced in intensity much more considerably after the longer reaction time [spectrum (*b*)] from that observed for [Ni(acac)$_2$]$_3$. Analysis (Fig. 2) showed a reduction in the Ni–O coordination number [4.4(4) at 1.97(1) Å], but a maintenance of an Ni···Ni shell [1.3(1) Ni···Ni at 3.09(1) Å]. In addition a new light-atom shell could be ascribed to 2.5(6) Ni–C at 2.16(3) Å. This data shows a mean structure of a similar nature to that of the trimeric catalyst precursor, but with partial substitution of the acac ligands by alkene and alkyl ligands. A structure such as that of **2** in which the bridging β-diketonate ligands are retained is consistent with these results, and could be an intermediate in the formation of **1**.

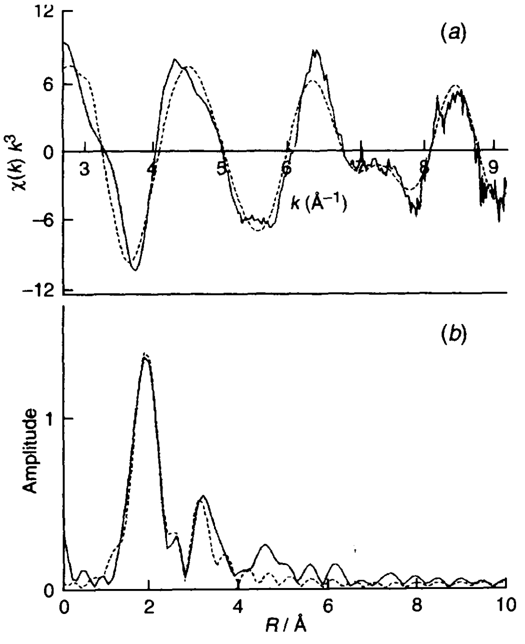
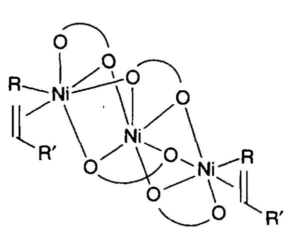


Fig. 2 EXAFS analysis of the [Ni(acac)$_2$], AlEt$_2$(OEt) (Ni : Al = 1 : 2) and hex-1-ene (Ni : hexene = 1 : 20) solution after 4.75 min at 0 °C. Average of 100 scans of 20 ms. (*a*) EXAFS and (*b*) Fourier-transform with (—) experimental and (---) calculated curves.



2

These experiments show that discussions of the mechanisms of alkene oligomerisation should include reversible trans-metallation processes. Perhaps more importantly, they show that EDE can provide good quality EXAFS data in timescales of the order of 0.1–10 s at the present time. Only the near-edge structure has normally been monitored this way;[9] there is only one previous report of EXAFS studies by EDE, that being on a heterogeneous palladium catalyst.[10]

We wish to thank the SERC and BP for a CASE award (J. M. C.), EPSRC and BP Chemicals also for a CASE award (V. L. K.), the University of Sydney for a Postgraduate Scholarship (D. N. McL.) and the Head of the Daresbury Laboratory for access to facilities.

Footnote

† Scanning XAS spectra were recorded on Station 7.1 at the SRS at the Daresbury Laboratory operating at 2 GeV with fluorescence detection with a Tl–NaI scintillation detector. EXAFS analysis used background subtraction and curved wave analysis procedures as previously described.[1–3] Global errors in distance determination have been estimated as 1.5%[6] and for coordination numbers 10–30%.[7]

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Received, 10th December 1995; Com. 5/07824E